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US 3692602 A

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(54) **Plastics laminate containing foamed polypropylene**

(57) A plastics laminate of substantially uniform thickness, comprises:

two outer layers each of a polymeric material; and
one or more inner layers including a core layer of a substantially uniformly foamed polypropylene:

in which the polymeric material has a higher melt flow index than the foamed polypropylene, and in which each layer is substantially free from filler.

The absence of filler means that the product can be recycled.

The laminate may be used to seal retort foods.

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PLASTICS LAMINATE AND ITS PRODUCTION

This invention relates to plastics laminates and to their production, e.g. by coextrusion. The laminate is suitably of a type that can be used to seal retort foods.

By way of example, plastics laminates are produced by coextrusion, to provide multi-layer sheeting used in the manufacture of packages and containers providing a barrier to the ingress or egress of moisture or gas. Such multilayer materials are used in the production of containers for, inter alia, retort foods. The seal is adapted to provide extended keeping properties for foods packed in the container. A filled, hermetically-sealed container may be subjected to elevated temperature for a time sufficient to ensure that its contents are sterile.

Polypropylene is a relatively inexpensive material, e.g. with respect to polystyrene. Polypropylene also possesses greater temperature resistance than, e.g. polystyrene, a desirable property for high temperature food processing and product reheating. This material is therefore potentially of great value in the production of plastics laminates. However, fillers and/or modifiers are often included, to improve the melt strength of the material.

EP-A-0287826 describes a thermoplastic resin article comprising two outer layers, each of an unfoamed thermoplastic resin, and a foamed inner layer. Polypropylene is one example of the polymers that can be used to prepare such a three-layer structure. In order to prevent "corrugation" as the laminate expands following extrusion from a die, it is considered essential for the outer (or facing) layers to include a filler in an amount of 10 to 400 parts by weight per 100 parts by weight of the thermoplastic resin in each cover layer.

WO-A-9113933 discloses a thermoformable, rigid or semi-rigid polypropylene foam sheet having a smooth surface and uniform cell structure. It is prepared by extruding a mixture of a nucleating agent such as citric acid-sodium bicarbonate, talc or titanium dioxide, a physical blowing agent such as a (halo)hydrocarbon, and a polypropylene resin having high melt strength and high melt elasticity.

After extrusion into a sheet, it is conventional practice to form and trim circular pieces of a plastics laminate, from the sheet, to provide containers for, say, retort food containers. The remainder of the sheet, which may constitute 20 to 50% of the extruded material, is essentially valueless.

It has now been found that laminates that are eminently satisfactory for sealing containers can be produced by coextrusion, relatively economically, because the "scrap" material is suitable for reincorporation into more such laminate. To this end, a novel plastics laminate comprises two outer (or facing) layers, each of a suitable polymeric material, and a core layer of a substantially uniformly foamed polypropylene, (and also, if necessary or desired, other inner layers), in which each layer contains no more than a minor amount of filler.

The novel laminate is of substantially uniform thickness. The facing layers have mechanical properties that are sufficient to prevent corrugation of the laminate to any unacceptable extent, on extrusion from a die. The polymeric material of each facing layer may be, for example, polypropylene or a copolymer of propylene and ethylene.

The thickness of each facing layer is preferably 50 to 500 μm, more preferably 150 to 300μm. The foamed core layer between the facing layers is generally thicker, e.g. 400 to 2000 μm and more preferably 700 to 1300μm. The density of the core layer may be 10 to 50% less than when unfoamed and/or than each facing layer.

The core layer comprises foamed polypropylene. This layer may be generally of the type described in EP-A-0287826 or WO-A-9113933. The critical physical property of a polypropylene grade suitable for foaming, is melt strength. The melt strength must be sufficient for successful closed cell foaming. This usually results in a grade with a melt flow index less than 1.5 unless it is a modified grade with high melt strength properties.

While the skilled man can select suitable material for the facing layers, the melt flow index should be higher than, preferably between two and four times, e.g. 3 times, that of the polypropylene being foamed. This allows sufficient strength to protect the foam layer from breaking through the surface, but also allows the material to flow adequately to the full sheet width, when in the die.

In order to provide the laminate with desirable characteristics, the cells of the foam should be substantially uniform, e.g. of an average size 50 to 400 μm in diameter. Substantial uniformity can be achieved by control of the coextrusion conditions and the choice of a blowing agent having a suitable particle size. It is apparently unnecessary to use both a nucleating agent and a blowing agent; any of the chemical foaming agents disclosed in EP-A-0287826 can be used, e.g. azodicarbonamide or a sodium citrate-sodium bicarbonate mixture.

Apart from any foaming agent, the core layer is usually free of filler or any other inorganic material, since this may mitigate against the production of a uniform foam. Further, it is unnecessary for either facing layer to include any inorganic material, although a very minor amount of inorganic material may be present. The use of up to 1 or 2% by weight of a filler such as talc or calcium carbonate is not precluded, but a similar or slightly higher amount, but usually less than 7% by weight with respect to the polymeric material, of a pigment may be

present if desired. A suitable pigment is titanium dioxide, but any conventional pigment may be used.

The absence of filler has several advantages in addition to reusability. These include reduced stiffness, reduced hygroscopicity, higher gloss and improved qualities as a substrate for printing, reduced bulk density, improved sheet infrared heating and reduced sag near heating elements of the type used in a thermoformer.

A laminate of the invention may comprise three layers only, i.e. consisting of one core layer in addition to the two facing layers. However, especially when the laminate is to be used as a container, there will generally be additional layers, depending on the particular requirements. For shelf-stable foods, another inner layer that may be present is of an oxygen-barrier material that is suitably 40 to 250 μm thick. This may be of any conventional type, a preferred example being ethylene-vinyl alcohol copolymer (EVOH). This material may include a minor amount of filler, e.g. mica, of the type conventionally used to enhance the barrier effect. As is well known, EVOH and other materials that may be included in a laminate of the invention may require the use of tie layers on either face, in order to prevent delamination from the adjacent layers.

Particular examples of laminates of this multi-layer type are the following:

facing layer	facing layer
core layer	core layer
tie layer	tie layer
oxygen barrier material	oxygen barrier material
tie layer	tie layer
facing layer	core layer
	facing layer

A very important aspect of the present invention is that the material is reusable, owing to the lack or at most low content of inorganic material. Accordingly, the core layer may comprise, in an amount of up to 95% by weight

thereof, material derived from a laminate of the invention. In this modification, therefore, the core layer comprises primarily polypropylene but also other polymers such as any copolymer used in the facing layer and any EVOH or other material that may be present in addition to the core and facing layers.

A laminate of the invention is produced by coextrusion of the various layers through an extrusion die. The materials are fed into the die and subjected to decreasing temperature. Between the point at which they melt and the point at which they are extruded (at the die manifold), the foaming agent is activated so that the core layer expands. The shape of the die must accommodate this expansion, and means may be provided to pull out CO_2 or any other gas, but the process is conducted so that there is no pressure drop, and preferably a gradual increase in pressure, between the given points. The extruded sheet cools at the die, so that its viscosity increases. It may be taken up on a polished roll.

As indicated above, the extruded laminate can have individual shapes formed and trimmed in conventional manner, but the remainder of the sheet can be reused. For this purpose, it is ground, e.g. to a particle size of less than 10 mm^3, and this "regrind" material can be recirculated directly for addition to the core material as supplied to the extrusion die. The amount of "regrind" in the core material will not usually be more than 95% by weight thereof. Any entrapped gas can be removed by using a multi-stage screw, prior to re-introducing additional blowing agent. Another option is to mix the blowing agent into the regrind prior to feeding into the extruder. This blowing agent should possess a decomposition temperature greater than the melting point of the polypropylene grade.

The following Example illustrates the invention.

Example

A seven layer structure was prepared, of four types of material, as follows:

1. Two-cap layers (top and bottom) each of which accounts for 15% of the total thickness. These layers are a polypropylene copolymer possesssing a melt flow index of 2.

2. Two buffer layers, each of which accounts for 30% of the total sheet thickness. Each layer comprises 50% by weight of a polypropylene copolymer (M.F.I. = 0.6), 49% of reground sheet of the same type as described here, and 1% of a bicarbonate-citric acid-type foaming agent.

3. Two adhesive layers each of which accounts for 2% of the total sheet thickness.

4. A central oxygen barrier layer, account for 6% of the total sheet thickness, of ethylene-vinyl alcohol.

The total sheet thickness is 1500 μm.

The sheet is made on a co-extrusion line utilising a combination of 63 mm (2.5") and 90 mm (3.5") single-screw extruders. These feed into a feedlock which combines the layers before feeding a manifold die. The sheet is then cooled using a polished roll stack.

The extruder processing the foamed material is of the two-stage type, with a vent hole half way along the barrel.

The processing temperatures along the path of the buffer (foamed) layer are:

Extruder rear zones	-	200°C
Extruder middle zones	-	210°C
Extruder front zones	-	220°C
Feed tubes	-	220°C
Feed block	-	210°C
Die	-	200°C

The material emits the die through a gap of 1.5 mm at a rate of 400 kg/hr.

The average diameter of the foam cells in the finished sheet is 100 μm, and the density of the foam layers is 0.6 g/cm^3.

CLAIMS

1. A plastics laminate of substantially uniform thickness, comprising:

two outer layers each of a polymeric material; and

one or more inner layers including a core layer of a substantially uniformly foamed polypropylene;

in which the polymeric material has a higher melt flow index than the foamed polypropylene, and in which each layer is substantially free from filler.

2. A laminate according to claim 1, which comprises, in sequence between the outer layers, a core layer, a layer of an oxygen-barrier material and, optionally, a further core layer.

3. A laminate according to claim 2, in which the oxygen-barrier material is an ethylene-vinyl alcohol copolymer.

4. A laminate according to claim 3, in which the oxygen-barrier material layer is 40 to 250 µm thick; and each outer layer is 50 to 500 µm thick.

5. A laminate according to any preceding claim, in which either or each outer layer includes a pigment in an amount of less than 7% by weight of the polymeric material.

6. A laminate according to any preceding claim, in which the melt flow index of the polymeric material is 2 to 4 times that of the foamed polypropylene.

7. A laminate according to any preceding claim, in which the polymeric material is a homopolymer or copolymer of propylene, and the core layer comprises up to 95% by weight thereof of material derived from such a laminate.

8. A process for producing a laminate as defined in any of claims 1 to 7, which comprises coextruding the layers through an extrusion die substantially without any pressure drop between the melting of the plastics materials and the die manifold.

9. A process according to claim 8, in which the core layer as supplied to the die includes a solid chemical foaming agent whose particle size is 5 to 50 μm.

10. A process according to claim 8 or claim 9, in which the core layer as supplied to the die comprises, in an amount of up to 95% by weight thereof, particles obtained by grinding a laminate according to any of claims 1 to 7.

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

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Relevant Technical fields

(i) UK Cl (Edition L) B5N

(ii) Int Cl (Edition 5) B32B

Search Examiner
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Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI, CLAIMS

Date of Search
22 APRIL 1993

Documents considered relevant following a search in respect of claims 1 TO 10

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	WO 91/13933 A1 (JAMES RIVER) - eg page 18 line 3 to page 20 line 19, particularly page 18 lines 12 to 15	at least 1,2,3,8
X	US 3692602 A (OKADA) - eg Example 8	at least 1,7,8
A	GB 2211191 A (SEKISUI) - eg Example 8	1
A	EP 0287826 A2 (MITSUBISHI) - eg Examples	1

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

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